

반응표면법을 이용한 티타니아가 도입된 PEI-PVAc 복합막의 CO₂/CH₄ 분리 효율 최적화

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Optimization of CO₂/CH₄ Separation Efficiency of Titania Incorporated PEI-PVAc Composite Membranes through Response Surface Methodology

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Abstract: This study examines the optimization of CO₂/CH₄ separation utilizing polyetherimide (PEI)-polyvinyl acetate (PVAc) blend membranes augmented by TiO₂ nanoparticles. This study utilizes membrane-based separation procedures, preferred over traditional methods due to their environmental and economic advantages. The gas permeance and selectivity of the membranes were evaluated using a custom gas permeation unit, with variations in temperature, pressure, and nanoparticle composition. A combination of response surface methodology (RSM) and central composite design (CCD) was utilized to forecast and enhance the process elements influencing separation efficiency. The research indicates that TiO₂ nanoparticles markedly improve the separation efficiency of membranes, with the ideal concentration determined to maximize CO₂ permeance while decreasing CH₄ permeance. The experimental results confirmed the predictive accuracy of the created models, evidenced by a R² value of 0.9813, indicating a strong fit. The results highlight the promise of nanoparticle-enhanced membranes in industrial applications.

Keywords: response surface methodology, optimization, blend membrane, composite membrane, CO₂ separation.

Introduction

Natural gas is a vital energy resource, contributing approximately 22% to the global energy supply. However, it often contains carbon dioxide (CO₂) as an impurity, which lowers its calorific value and affects overall energy efficiency.¹ The CO₂ in natural gas reacts with water, creating acidic conditions that can damage pipelines and infrastructure.² Therefore, removing CO₂ from natural gas is crucial for environmental protection and maintaining its energy value. This has made CO₂ removal a key focus of scientific research, particularly in light of the expected rise in natural gas use and the need to meet pipeline standards.^{3,4}

Due to their smaller environmental impact, cleaner produc-

tion, cost-effectiveness, and energy efficiency, membrane-based separation processes are now preferred over traditional methods like solid adsorption, liquid absorption, and cryogenic distillation.⁵ The utilization of membrane technology for CO₂/CH₄ separation has garnered significant attention in various fields, including natural gas sweetening, biogas purification, and water treatment. This technique ensures a high methane recovery rate of over 96% and the ability to capture and reuse pure CO₂.⁶ Nevertheless, a notable obstacle with commercial membranes, whether organic or inorganic, is finding the right equilibrium between gas permeability and selectivity.⁷

Polymer blends are a viable approach for producing gas separation membranes. The fundamental problem with this strategy is to ensure compatibility amongst the polymers utilized while preserving essential mechanical qualities.⁸ The compatibility can be enhanced by incorporating nanoparticles into polymer blends to enhance their physical and chemical characteristics

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and promote compatibility. For instance, adding TiO₂ nanoparticles to a polyetherimide (PEI)-polyvinyl acetate (PVAc) blend has been demonstrated to improve the blend's mechanical durability and reduce solvent precipitation, resulting in denser membrane layers and better separation capabilities.⁹

Li *et al.* found that adding TiO₂ nanoparticles to polymer membranes enhanced their mechanical stability.¹⁰ Furthermore, they discovered that adding TiO₂ reduced the rate of solvent precipitation, resulting in a thicker membrane cross-section skin layer. In addition, Madaeni *et al.* observed improved separation properties and a related increase in the thickness of the membrane wall when TiO₂ nanoparticles were added.¹¹ Similarly, adding TiO₂ nanoparticles to the PVAc matrix increased the performance and thermal stability of the produced membranes.¹² The gas separation performance of the poly(amide-imide)-TiO₂ nanocomposite membrane surpassed that of pure poly(amide-imide), even with a low TiO₂ loading.¹³

The above-mentioned studies evaluated the incorporation of titania fillers and assessed the physical, mechanical, and separation performance of the membranes. However, the influence of process parameters on membrane performance has not been examined in detail. Notably, operating temperature affects the free volume and flexibility of the polymer matrix, typically enhancing gas permeance while reducing selectivity. Conversely, higher feed pressures can diminish the sorption capacity and gas solubility of the materials, potentially impairing their overall performance.^{1,2}

Therefore, in this study, a thorough investigation has been carried out to examine the effect of temperature, total pressure difference, and TiO₂ composition on the permeability of CO₂ and CH₄ and the separation factor between CO₂ and CH₄. The analysis utilized response surface methodology (RSM) and central composite design (CCD) to determine the optimal settings for achieving minimum CH₄ permeance and maximum CO₂ permeance and separation factor.

Experimental

Materials. PEI pellets (melt flow index, 9 g/10 min), PVAc beads (density, 1.19 g/cm³ at 25 °C), N-methyl-2-pyrrolidone (NMP, 99.5% purity), and TiO₂ nanoparticles (primary particle size 21 nm) were all sourced from Sigma Aldrich (St. Louis, MO, USA).

Membrane Development. By employing a casting knife, the membrane solution was uniformly applied onto a glass plate, forming a film with a thickness of 150 μm. The mem-

branes fabricated in this research included blend polymer and composite membranes, as previously described in our studies.^{14,15} The blend membrane consists of a blend ratio of 98:2 for PEI-PVAc. Subsequently, TiO₂ was introduced as a nano-filler into the blend polymer dope solution to develop composite membranes. The titania content was also adjusted from 0 to 2 wt%. The newly formed membranes were chilled in a water bath after casting. The membranes were immersed in distilled water for three days to ensure that all solvent was completely removed. Following that, they were allowed to air dry at room temperature.

Gas Permeation Study of the Developed Membranes: The developed membranes underwent gas permeation and ideal selectivity analysis. For this analysis, CO₂ and CH₄ gases were utilized, with variations in feed pressure and temperature as outlined, Table 1. The data is categorized into input parameters, including permeate temperature, feed pressure, and TiO₂ composition. In contrast, the responsive parameters included the gas permeation rates of CO₂ and CH₄ and the ideal gas selectivity (CO₂/CH₄).

Using a specifically made gas permeation machine for these measurements and determined by the equations, permeability testing for pure gases was carried out on the developed membranes,¹⁵ Equations 1 and 2.

$$P_x/l = \frac{Q}{A\Delta P} \frac{273.15}{T} \quad (1)$$

$$\alpha_{xy} = \frac{P_x}{P_y} \quad (2)$$

Gas permeance (P_x/l) is quantified in GPU, where 'x' in the subscript denotes the incident gas, such as CO₂ or CH₄. Here, 'Q' indicates the volumetric flow rate, and 'A' represents the membrane's effective surface area. The permeation occurs under a specific pressure difference and at a designated temperature (T). The ratio of the competing incident gases' x and y permeabilities through the membrane is ideal selectivity or α_{xy} .

Optimization Strategy by Using RSM: This work used Design of Experiments (DoE) to investigate CO₂ separation and process optimization with PEI-PVAc blend membranes in a methodical manner. A collection of statistical and mathematical methods known as RSM are used to model and analyze situations in which multiple variables affect an interest response. The objective was to maximize that response.

As extensively documented in the literature, the advantages of employing this method include reducing the number of experimental runs, determining optimal operating conditions for scale-up, and understanding the interactions among differ-

Table 1. Experiment Design Matrix and Results for Responses

No Exp.	Factors			Responses		
	Pressure (bar)	Temperature (°C)	TiO ₂ Composition (wt%)	CO ₂ Permeance (GPU)	CH ₄ Permeance (GPU)	Selectivity (CO ₂ /CH ₄)
1	2	25	0	14.86	0.49	30.33
2	4	25	0	14.08	0.5	28.16
3	6	25	0	14.12	0.51	27.69
4	2	25	1	17.31	0.52	33.29
5	4	25	1	17.04	0.51	33.41
6	6	25	1	16.9	0.52	32.50
7	2	25	2	19.72	0.48	41.08
8	4	25	2	19.26	0.51	37.76
9	6	25	2	18.93	0.49	38.63
10	2	35	0	12.01	0.53	22.66
11	4	35	0	11.26	0.56	20.11
12	6	35	0	10.89	0.58	18.78
13	2	35	1	15.02	0.47	31.96
14	4	35	1	14.14	0.48	29.46
15	6	35	1	14.01	0.5	28.02
16	2	35	2	16.31	0.5	32.62
17	4	35	2	15.52	0.51	30.43
18	6	35	2	15.02	0.53	28.34
19	2	45	0	10.42	0.58	17.97
20	4	45	0	10.01	0.57	17.56
21	6	45	0	9.31	0.59	15.78
22	2	45	1	12.98	0.46	28.22
23	4	45	1	12.05	0.47	25.64
24	6	45	1	11.46	0.49	23.39
25	2	45	2	14.28	0.53	26.94
26	4	45	2	13.92	0.56	24.86
27	6	45	2	13.11	0.55	23.84

ent experimental variables.

The dataset encompasses pressure, temperature, and TiO₂ composition, aiming to maximize CO₂ permeance. A quadratic model was applied to the data, integrating both linear and interaction terms of the variables, which aids in elucidating the combined effects of pressure, temperature, and TiO₂ composition on CO₂ permeance.

Similarly, a quadratic model defined the relationship between the variables and selectivity, incorporating linear and interaction effects. This approach provides a comprehensive insight into how each variable impacts the outcome, enhancing understanding of their collective influence on selectivity.

Results and Discussion

The experimental results generated using RSM in combination with CCD are presented along with the corresponding outcomes, Table 2. The CO₂ and CH₄ permeance ranged from 9.31 to 19.72 GPU and 0.46 to 0.59 GPU, respectively. Furthermore, CO₂/CH₄ separation coefficients ranging from 15.78 to 41.08 were attained.

The quadratic model, incorporating coded factors, is recommended by the DoE software for analyzing CO₂ permeance, Equation 3.

Table 2. Ranges of Process Parameters and Their Variations Over the Developed Membranes

Variables	Factor code	Level and range (coded)		
		-1	0	1
Feed pressure (bar)	A	2	4	6
Temperature (°C)	B	25	35	45
TiO ₂ composition (wt%)	C	0	1	2

$$Y = \beta_0 + \beta_1A + \beta_2B + \beta_3C + \beta_{12}AB + \beta_{13}AC + \beta_{23}BC + \beta_{11}A^2 + \beta_{22}B^2 + \beta_{33}C^2 \quad (3)$$

CO₂ Permeance. ANOVA outcomes and empirical model factors for CO₂ permeance are highlighted, Table 3. CO₂ selectivity models using both coded and real components are provided, Equation 4.

Based on the data in Table 3, the model's F-value is 437.438, and the associated P-value, less than 0.05, suggests that the model is statistically significant.

$$\text{CO}_2 \text{ Permeance} = 27.23 - 0.2049A - 0.6332B + 4.1528C - 0.0078AB - 0.0117AC - 0.0273BC + 0.0292A^2 + 0.0063B^2 - 0.4883C^2 \quad (4)$$

Furthermore, while terms such as A² and AC were found to be insignificant, they have been included to maintain the hierarchical structure of the model, Equation 4. Additionally, an R² value of 0.996 confirms the model's high accuracy in predicting CO₂ permeance. Regarding the individual effects, the composition of TiO₂ (referred to as term C) had the most notable

influence on CO₂ permeance, as indicated by the greatest F-value of 262.91. Temperature (term B) and gas feed pressure (term A) had F-values of 111.349 and 6.693, respectively, suggesting a lesser impact. These results underscore the predominant influence of TiO₂ composition on CO₂ permeance. Meanwhile, the second order (AC and BC) and quadratic terms (A², B², and C²) were found to have minimal impact on the CO₂ permeance for blend membranes.

The effect of temperature, feed pressure, and the TiO₂ feed content on the permeance of CO₂ in polymer composite membranes (PCMs) are presented in Figure 1. Figure 1(a) shows a notable decrease in CO₂ permeance as feed pressure increases, consistent with previous studies suggesting a gas permeability reduction for polarizable gases like CO₂ in glassy polymers under elevated pressures.¹⁶ This decline supports the dual-mode sorption hypothesis and is further influenced by membrane matrix contraction, which reduces the membrane's swelling effect, consequently lowering CO₂ permeability.^{15,17} Furthermore, as temperature rises, CO₂ diffusivity through the membrane increases, contributing to a minor decrease in CO₂ permeance. However, this decrease is counteracted by reducing adsorption coverage as fewer CO₂ molecules absorb to the membrane surface.¹⁸ The highest recorded CO₂ permeance at 25 °C and 2 bar was 17.31 GPU, while the lowest at 45 °C and 6 bar was 11.46 GPU.

The effects of temperature and TiO₂ composition on CO₂ permeance at 4 bar are highlighted, Figure 1(b). There is an observed increase in CO₂ permeance with higher TiO₂ composition, with a permeance of 19.26 GPU at 2 wt% TiO₂ and

Table 3. ANOVA Results and Empirical Model Terms of CO₂ Permeance

Sources	Sum of square	DOF	F-Value	PR (>F)	Mean Square	Significance
A	0.345	1	6.693	0.0192	0.349	S ^a
B	5.816	1	111.349	7E-09	5.817	S
C	13.734	1	262.916	8.94E-12	13.734	S
A ²	0.0817	1	1.563	0.228	0.082	N-S ^b
B ²	2.407	1	46.072	3.17E-06	2.407	S
C ²	1.431	1	27.391	6.74E-05	1.431	S
AB	0.288	1	5.519	0.0312	0.288	S
AC	0.007	1	0.125	0.728	0.0065	N-S
BC	0.897	1	17.163	0.0007	0.897	S
Residual	0.888	17	-	-	0.052	N-S
R ²	0.996	-	-	-	-	-
Adjusted R ²	0.993	-	-	-	-	-
Model	205.655	9	437.438	2.61E-18	22.851	S

^aSignificant. ^bNot Significant.

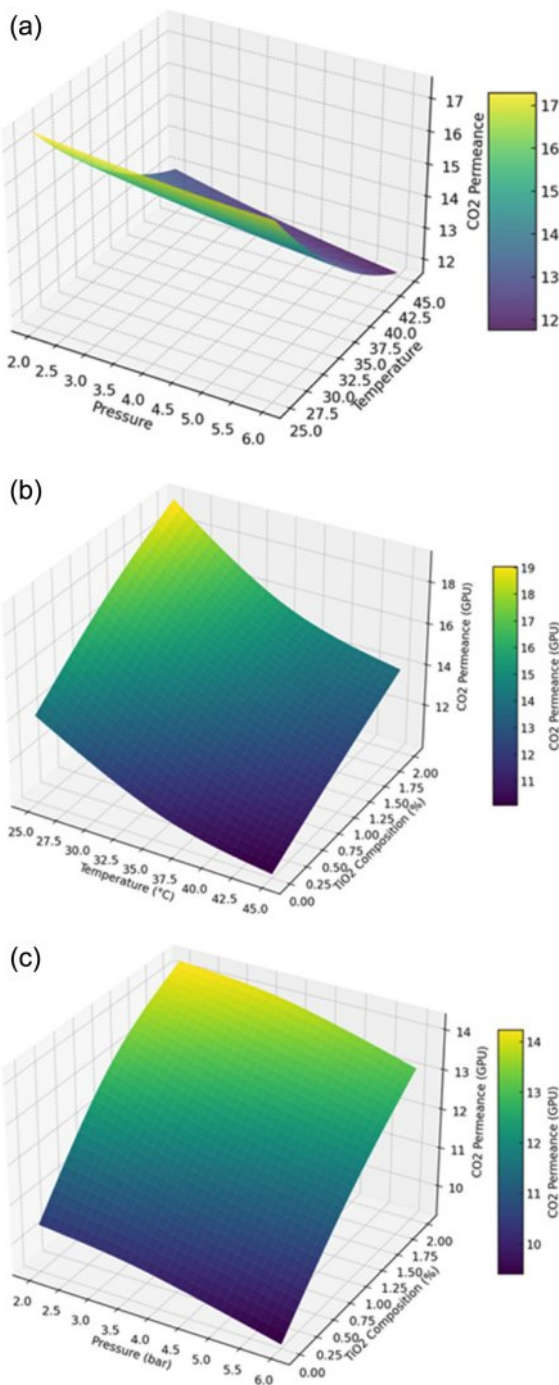


Figure 1. (a) Effect of temperature and pressure on CO₂ permeance at TiO₂ composition of 1 wt%; (b) effect of temperature and TiO₂ composition on CO₂ permeance at 4 bar pressure; (c) effect of pressure and TiO₂ composition on CO₂ permeance at a temperature of 45 °C.

25 °C. The addition of TiO₂ positively affects the CO₂ permeance, enhancing it by 36% at 2 wt% compared to the neat sample due to nanoparticle aggregation and void formation at the TiO₂-polymer interface, which facilitates gas diffusion.¹⁹ It also

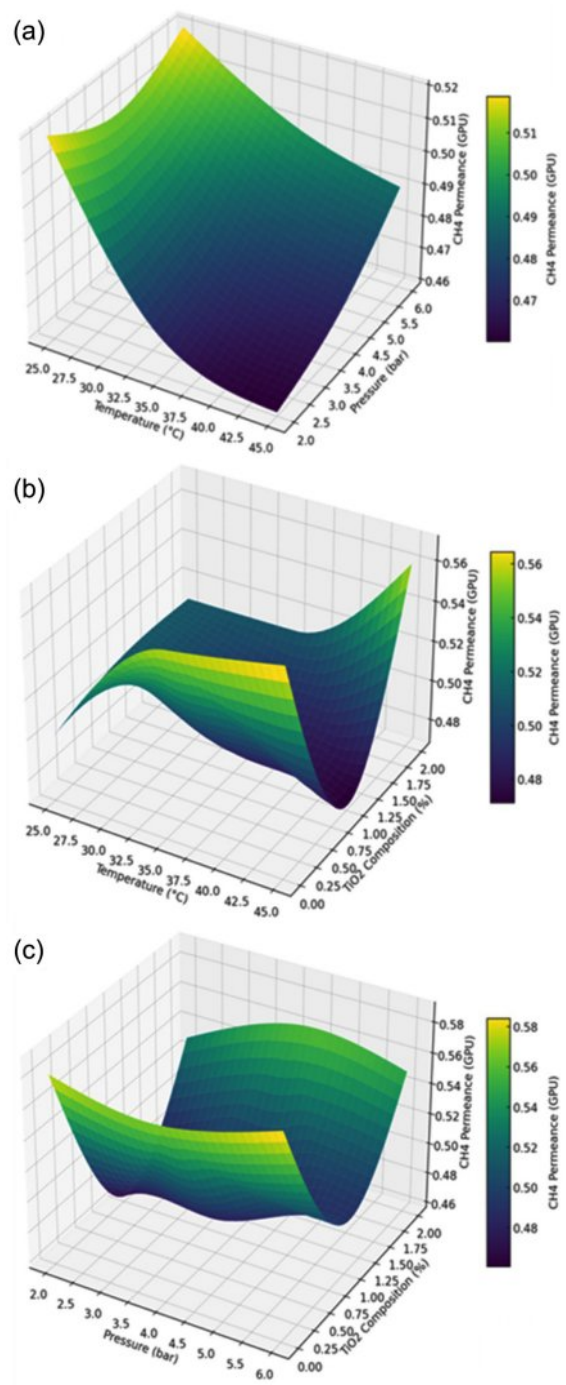


Figure 2. (a) Effect of temperature and pressure on CH₄ permeance at TiO₂ composition of 1 wt%; (b) effect of temperature and TiO₂ composition on CH₄ permeance at 4 bar; (c) effect of pressure and TiO₂ composition on CH₄ permeance at a temperature of 45 °C.

indicates that the trend of decreasing CO₂ permeance with rising temperature mirrors the observations, Figure 1(a), with the lowest permeance of 9.31 GPU at 45 °C in the absence of TiO₂ nanoparticles.

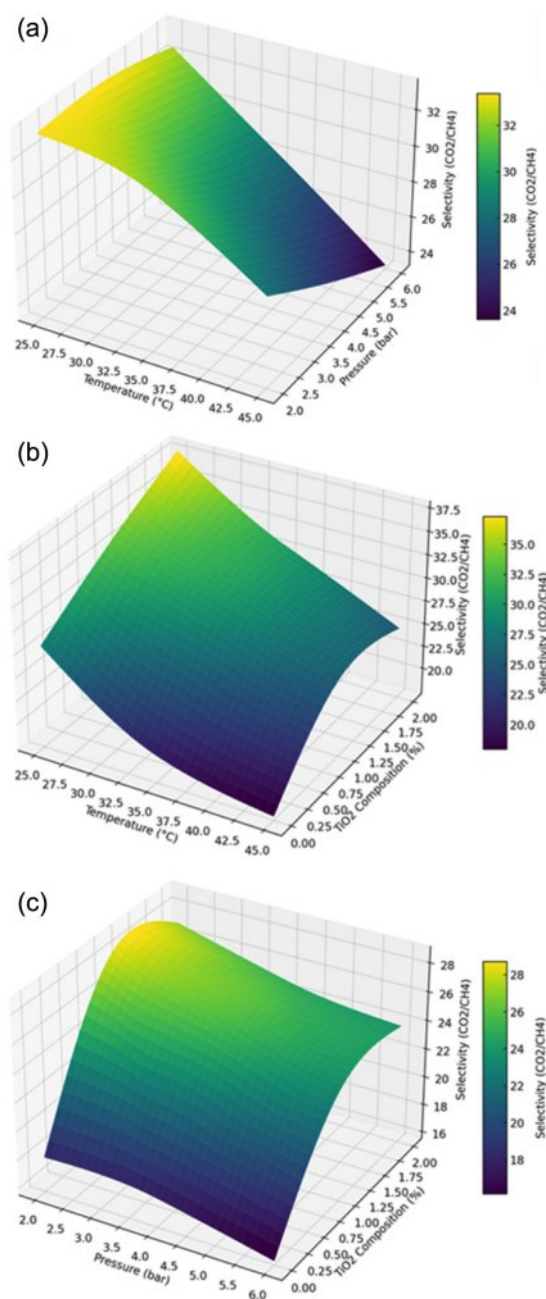


Figure 3. (a) Effect of temperature and pressure on selectivity (CO₂/CH₄) at TiO₂ composition of 1 wt%; (b) effect of temperature and TiO₂ composition on selectivity (CO₂/CH₄) at 4 bar pressure; (c) effect of pressure and TiO₂ composition on selectivity (CO₂/CH₄) at temperature of 45 °C.

The effects of pressure and TiO₂ composition on CO₂ permeance at 35 °C are shown in Figure 1(c). At this temperature, dual-sorption characteristics and thermodynamic interactions between the polymer matrix and the permeating gas work together to reduce CO₂ permeance in response to increased feed

pressure. The increase in CO₂ permeance with TiO₂ content at 35 °C is consistent with findings from Figure 3, showing a maximum permeance of 16.31 GPU at 2 bar and 2 wt% TiO₂, while the minimum permeance is 10.89 GPU at 6 bar for the blend membrane.

CH₄ Permeance. The mathematical representations for CH₄ permeance using real variables and coded components is presented, Equation 5. The empirical model terms and ANOVA findings for CH₄ permeance are shown in Table 4. The results demonstrate that the quadratic model is statistically significant for CH₄ permeance, as evidenced by its F-value of 2.596.

However, the terms including A, B, AB, AC, BC, A², and B² are found to be insignificant. The temperature appears to have the most impact on CH₄ permeance across the membrane, as indicated by the highest F-value of 14.409 for term C. Furthermore, the divergence between the experimental data and the anticipated CH₄ permeance is confirmed to be within an acceptable range by an R² value of 0.579. Nevertheless, the CH₄ model demonstrates lower predictive accuracy compared to the CO₂ model, the overall optimization strategy remains robust. This robustness is largely attributed to the fact that the optimization is primarily governed by separation performance, which is more strongly influenced by the CO₂ permeance model.

$$\begin{aligned} \text{CH}_4 \text{ Permeance} = & 0.4644 + 0.0042A + 0.0013B - 0.0683C \\ & + 0.0001AB - 0.0008AC - 0.0007BC - 0.0003A^2 + 0.000B^2 \\ & + 0.0406C^2 \end{aligned} \quad (5)$$

The 3D graphs illustrate the effect of TiO₂ temperature, composition, and pressure on the permeance of CH₄ in the PCMs, Figure 2. The behavior of CH₄ permeance in response to increasing temperature and feed pressure is analogous to the CO₂ permeance, Figure 2(a). As temperature decreases, CH₄ permeance rises gradually, reaching a maximum of 0.52 GPU at 25 °C and 6 bar. Conversely, an increase in feed pressure diminishes the dual-sorption properties and increases the diffusion properties of CH₄ through the available free volume, leading to a slight rise in CH₄ permeance.

CH₄ permeance decreases modestly with rising temperature due to the reduced solubility of the gas across the membrane surface as temperature increases, Figure 2(b). On the other hand, the addition of TiO₂ has an abrupt decrease in CH₄ permeance of nearly 1 wt% titania, and then a sudden increase is observed as well. This effect is prominent at a temperature of 45 °C. Furthermore, the increase in feed pressure affects the dual-sorption characteristics and CH₄ solubility coefficient, which leads to a decrease in CH₄ permeance. These results are com-

Table 4. ANOVA Results and Empirical Model Terms of CH₄ Permeance

Sources	Sum of squares	DOF	F-Value	PR(>F)	Mean Square	Significance
A	8.9E-05	1	0.102	0.753	8.9E-05	N-S ^b
B	1.5E-05	1	0.017	0.897	1.5E-05	N-S
C	1.2E-02	1	14.409	0.001	1.2E-02	S ^a
A ²	7.4E-06	1	0.009	0.927	7.4E-06	N-S
B ²	1.9E-06	1	0.002	0.964	1.9E-06	N-S
C ²	9.9E-03	1	11.379	0.004	9.9E-03	S
AB	7.5E-05	1	0.086	0.772	7.5E-05	N-S
AC	3.3E-05	1	0.038	0.847	3.3E-05	N-S
BC	5.3E-04	1	0.615	0.444	5.3E-04	N-S
Residual	1.5E-02	17	-	-	8.7E-04	N-S
R ²	0.579	-	-	-	-	-
Adjusted R ²	0.356	-	-	-	-	-
Model	0.020264	9	2.596	0.043	2.3E-03	S

^aSignificant. ^bNot Significant.

parable to those documented in the literature about CH₄ permeance in ZIF-8/6FDA-durene flat sheet MMMs.²⁰

The PCM with a TiO₂ content of 1 wt% at 2 bar had the lowest CH₄ permeance, measuring at 0.47 GPU. By contrast, the highest CH₄ permeance of 0.58 Gas Permeation Units (GPU) is achieved using the smallest amount of TiO₂ and a pressure of 6 bar, Figure 2(c).

CO₂/CH₄ Ideal Selectivity. The details of CO₂/CH₄ selectivity models expressed as coded and real factors, Equation 6. The model's statistical significance is demonstrated by its note-

worthy F-value of 42.495. Important terms A, B, BC, A², and C² in the model for CH₄ permeance. With an R² value of 0.957, this model depends on predicting the CO₂/CH₄ separation factor from the three variables involved.

The analysis further highlights the dominant influence of TiO₂ composition, which has the highest F-value of 51.546, indicating a substantial impact on the separation factor. This is followed by temperature and pressure, with F-values of 8.878 and 1.345, respectively, suggesting that while temperature also plays a notable role, the effect of pressure is relatively less sig-

Table 5. ANOVA Results and Empirical Model Terms of CO₂/CH₄ Selectivity

Sources	Sum of squares	DOF	F-Value	PR(>F)	Mean square	Significance
A	3.692	1	1.345	0.262	3.692	N-S ^b
B	24.365	1	8.878	0.008	24.365	N-S
C	141.464	1	51.546	0.000	141.464	S ^a
A ²	0.971	1	0.354	0.560	0.971	N-S
B ²	9.209	1	3.356	0.085	9.209	N-S
C ²	43.072	1	15.694	0.001	43.072	S
AB	1.500	1	0.547	0.470	1.500	N-S
AC	0.106	1	0.039	0.847	0.106	N-S
BC	4.057	1	1.478	0.241	4.057	N-S
Residual	46.655	17	-	-	2.744	N-S
R ²	0.957	-	-	-	-	-
Adjusted R ²	0.935	-	-	-	-	-
Model	1049.628	9	42.495	0.000	116.625	S

^aSignificant. ^bNot Significant.

nificant in determining the CO₂/CH₄ selectivity, Table 5. The ideal selectivity of the asymmetric membrane is affected by its dense selective layer and other process characteristics that significantly affect its performance.^{1,21}

$$\begin{aligned} \text{Selectivity} = & 55.4148 - 0.9194A - 1.2865B + 12.3309C \\ & - 0.0177AB - 0.0470AC - 0.0581BC + 0.1006A^2 + 0.0124B^2 \\ & - 2.6793C^2 \end{aligned} \quad (6)$$

The effect of pressure, temperature, and TiO₂ composition on the ideal selectivity is illustrated, Figure 3. The decrease in ideal selectivity with an increase in temperature, likely due to the reduced sorption properties of the more condensable CO₂ gas at higher temperatures, which diminishes its interaction with the membrane surface, leading to a decrease in ideal selectivity, Figure 3(a). The lowest CO₂/CH₄ separation factor observed is 23.39 at 45 °C and 6 bar. Furthermore, ideal selectivity also declines with increased feed pressure, correlating with a decrease in CO₂ permeance as pressure rises—a trend consistent with previous studies suggesting reduced gas permeability for polarizable gases like CO₂ under increased pressure in glassy polymers.²² The maximum separation factor recorded is 33.41 at 4 bar and 25 °C.

At a constant feed pressure of 4 bar, the effect of temperature and TiO₂ content on the CO₂/CH₄ separation factor is highlighted, Figure 3(b). The separation factor improves as TiO₂ composition rises from 0% to 2% by weight. The optimal selectivity of the PCMs is positively impacted by the addition of TiO₂, as gas flow through the membrane is improved by nanoparticle aggregation and void formation at the TiO₂-polymer interface. The highest ideal selectivity achieved is 41.08 at a TiO₂ composition of 2 wt% and a temperature of 25 °C. However, an increase in temperature at a TiO₂ composition of 2 wt% results in a decrease in ideal selectivity, with the minimum separation factor of 17.56 at 45 °C.

The effect of TiO₂ composition and pressure on the optimum selectivity of CO₂/CH₄ at a constant temperature of 35 °C. At 2 bar of pressure and 1.85 weight percent TiO₂, the maximum optimum selectivity of 32.62 is observed, Figure 3(c).

In contrast, the minimum ideal selectivity of 18.78 is noted at a pressure of 6 bar and in the absence of TiO₂ nanoparticles. These observations underscore the complex interplay of process parameters on membrane performance, particularly how material composition and operating conditions jointly dictate separation efficacy.

Comparison of Predicted and Actual Selectivity. The actual versus predicted selectivity derived from the quadratic

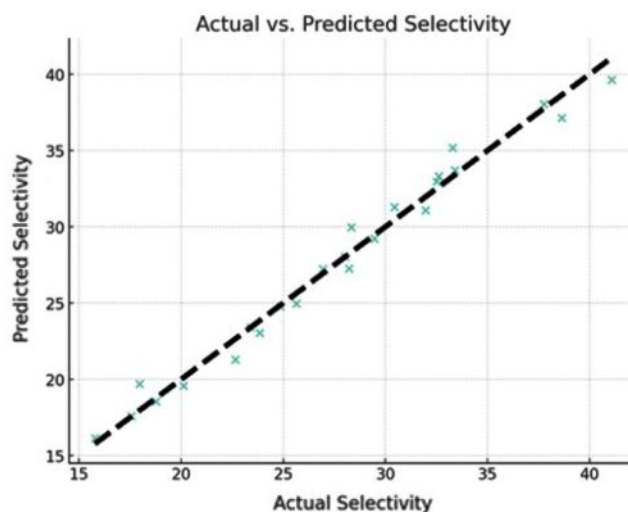


Figure 4. Comparison of actual and predicted selectivity values.

model employed in this study showed, Figure 4. The scatter plot points, which represent the actual selectivity values, are plotted against the predicted selectivity values from the model. The proximity of these points to the dashed line, which indicates a perfect correlation between the actual and predicted values, highlights the model's high prediction accuracy.

The model's intercept is approximately 29.75, with an R² value of 0.9813, indicating a strong fit of the model. The high R² score suggests that the model can explain a significant percentage of the variance in selectivity, which is crucial for accurate predictions and optimization. The image shows that the model accurately represents the complex relationship between the influencing variables (pressure, temperature, and TiO₂ composition) and selectivity. This supports the model's robustness and demonstrates its usefulness for optimization and prediction applications.

Conclusions

The study has effectively shown that separating CO₂ and CH₄ can be improved by utilizing membranes made from a blend of PEI-PVAc and TiO₂ nanoparticles. We established optimal conditions that considerably improve the separation performance of these membranes by using a quadratic model and strategically combining RSM and CCD. The experimental results closely match the predicted models, resulting in an R² value of 0.9813. This demonstrates a strong correlation and confirms the model's capability to manage the complex connections among process variables.

Adding TiO₂ nanoparticles to the membrane matrix has

demonstrated significant advantages in enhancing mechanical stability and separation efficiency. This nanoparticle addition improves the permeability of CO₂ and enhances its selectivity while preserving or reducing the permeability of CH₄ across different operational settings. The study also highlights the critical influence of temperature, pressure, and TiO₂ composition on membrane performance, providing detailed insights into how each factor contributes to overall efficiency.

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